

Title: Process for the removal of sulfur compounds from hydrocarbon feedstocks

The invention is directed to a process for the removal of sulfur compounds from hydrocarbon feedstocks, more in particular to the removal of thiophenic compounds from feedstocks comprising benzene and/or hydrocarbon resins.

5 In chemical processes, such as hydrogenation and/or dehydrogenation, often a problem presents itself in that the sulfur and/or sulfur components in the feedstocks negatively affects the lifetime of a catalyst used in the processes, especially in the case of nickel catalysts. To avoid this problem, much attention has been paid to the removal of sulfur compounds
10 from the gaseous or liquid feedstock prior to the actual hydrogenation and/or dehydrogenation. Further, the presence of sulfur is quite often undesirable in view of the intended use of the hydrogenated material.

An important system for the removal of sulfur compounds from hydrocarbon feedstocks is based on the adsorption of the sulfur compounds on
15 an adsorbent. Well-known adsorbents are for example a-nickel adsorbents. These nickel adsorbents generally are in the form of supported nickel metal crystallites.

Other systems that are known, are based on the adsorption of the sulfur compound on an metal oxide, resulting in a reaction between the metal
20 oxide and the sulfur compound, producing a stable metal sulfide.

In US-A 5,482,616 a process for the removal of sulfur compound is disclosed, wherein the sulfur compound is removed by contact with a combined adsorbent based on a metal oxide that forms stable metal sulfides under the reaction conditions, and a hydrogenating component, such as nickel or a
25 precious metal.

In US-A 5,223,470 a nickel on alumina catalyst has been described, which has been promoted with sulfur, for the selective hydrogenation of edible oils.

In general sulfur impurities are present in feedstocks as sulfides, mercaptans or thiophenes. However, in some feedstocks such as certain benzene feedstocks, middle distillates, gasoline, kerosene, MTBE and hydrocarbon resins, the sulfur impurities are for example present as higher thiophenes or other sulfur compounds having low reactivity (such as dimethylthiosulfonate). Examples of feedstocks that contain such sulfur compounds are feedstocks used in the production of various hydrocarbons and related compounds, such as benzene, toluene, MTBE, furfural and related compounds, hydrocarbon resins and the like.

Quite often, it is a requirement, that the treatment does not result in hydrogenation of the hydrocarbon feedstock. For example, in case sulfur compounds have to be removed from benzene, hydrogenation of the benzene would result in a decrease of yield of the process.

US-A 6,503,388 is directed to a process for hydrogenating feedstocks containing thiophenic impurities comprising contacting the feed with a combination of a platinum group catalyst and a nickel catalyst, whereby the amount of sulfur removed from the feed is considerably raised.

The capacity of a nickel adsorbent for sulfur compounds is in general in the order of magnitude of 14 wt.%. This number is valid in case the sulfur impurities are in the form of sulfides and/or mercaptans. However, in case the sulfur is in the form of higher S-compounds, such as thiophenic compounds, the capacity decreases to about 2 wt.%. As a result the amount of adsorbent that is required increases strongly when these sulfur compounds are present in the feedstock.

Accordingly, it is an object of the invention to provide a process for the removal of sulfur compounds from hydrocarbon feedstocks, more in particular to the removal of thiophenic compounds from feedstocks comprising

benzene and/or hydrocarbon resins, wherein the capacity of the adsorbent is increased, preferably to a value comparable to that for sulfides and mercaptans.

The present invention is based on the insight, that a nickel
5 adsorbent of which the nickel surface has been deactivated, meets this object, provided that the desulfurisation is carried out in the presence of hydrogen. More in particular it is important, that the nickel adsorbent has a remaining adsorption capacity for sulfur. This means that on the one hand, the adsorbent
10 should be sulfided in a sufficient amount to prevent hydrogenation of the hydrocarbon, while at the same time being able to adsorb heavier sulfur compounds, such as thiophenic sulfur compounds.

The invention is accordingly directed to a process for the removal of contaminating sulfur compounds from hydrocarbon feedstocks, said process comprising contacting the feedstock in the presence of hydrogen with a nickel
15 adsorbent, of which adsorbent the nickel surface has been deactivated with S or an S-compound. The invention is accordingly defined as a process for the removal of contaminating sulfur compounds, more in particular thiophenic sulfur compounds, from hydrocarbon feedstocks, said process comprising contacting the feedstock in the presence of hydrogen with a sulfided nickel
20 adsorbent, of which adsorbent the rate constant for tetralin hydrogenation activity at 150°C is less than 0.01 l/s.g cat and wherein in said adsorbent part of the nickel is present in the metallic form

The rate constant for tetralin hydrogenation, one of the essential features of the catalyst to be used in the present invention, is determined as
25 follows. In a micro-reactor the gas phase hydrogenation of tetralin is performed. A hydrogen flow of 50 cm³(STP)/min having a tetralin concentration corresponding to a saturation temperature of 13.6°C is led through a reactor at 150°C. The catalyst bed consists of 200 mg (0.1 - 2.0 cm³ of density 0.2 - 2.0 g/cm³) of catalyst in a sieve fraction of 30 - 60 mesh and diluted with inert

material in the same mesh size (at atmospheric pressure and GHSV of 30 – 300 1/h). The reaction products are analyzed in line with a gas chromatograph.

From the analyses the tetralin conversion is calculated.

(Conversion = (tetralin in – tetralin out)/tetralin in).

5 The calculation results in a rate constant k expressed as
1/s.g(catalyst).
($k = - \text{GHSV} * (\ln(1 - \text{conversion})) / \text{Weight}$).

The activity of the material to be used in the process of the invention should be such that the rate constant at 150 °C is less than 0.01 1/s.g cat. This
10 means in practice that almost no tetralin is hydrogenated.

This feature of the invention corresponds in general to a hydrogen adsorption capacity of less than 10 micro-moles/g.cat. measured with static hydrogen chemisorption at 50 °C (ASTM method D 3908-82).

An other important feature of the invention resides therein that part
15 of the nickel is present as metal. Preferably this is at least 10 %, on atomic basis. The upper limit of the amount of metallic nickel is determined by the fact that no unwanted hydrogenation of the feedstock occurs. This feature is determined in the first place by the tetralin rate constant and in a preferred embodiment by the requirement that the nickel surface has an atomic S to Ni
20 ratio of at least 0.5.

It is quite surprising that the process of the invention provides a good removal, as desulfurisation in the absence of hydrogen with merely a nickel adsorbent does not work, and desulfurization with a regular nickel adsorbent in the presence of hydrogen results in a run away of the reaction, as
25 hydrogenation of the feedstock occurs.

It is important to note that the process of the invention differs essentially from the well-known hydro desulfurization (HDS) processes. In these processes the sulfur containing feedstock is treated with a fully sulfided catalyst. The sulfur containing compounds are hydrogenated over the catalyst
30 and generally broken down to hydrogen sulfide, which is removed

subsequently. On an atomic basis, the amount of sulfur at the beginning of the catalyst bed and at the end, after the hydrogenation treatment is the same. Contrary thereto, the process of the present invention uses an adsorbent and results in a decrease of the sulfur content of the feedstock.

5 The invention is applicable for the removal of contaminating sulfur compounds from hydrocarbon feedstocks, more in particular those feedstocks described hereinabove.

 The invention can even be used for the treatment of feedstocks that contain unsaturation, which should not be hydrogenated. It has been found
10 that the process of the invention results in efficient removal of the contaminating sulfur compounds, without hydrogenation of the feedstock. However, in some instances, the condition may be adapted to obtain stabilisation of a feedstock, such as removal of gum precursors (styrene type compounds), which requires hydrogenation of some unsaturated components.

15 In a preferred embodiment of the invention the adsorbent is used in combination with a metal oxide adsorbent. The metal of the adsorbent is a metal that forms stable sulfides under the conditions applied in the process for the removal of contaminating sulfur compounds from hydrocarbon feedstocks. This metal oxide can either be used in the nickel adsorbent, such as described
20 in US-A 5,482,616, although the adsorbent does not necessarily has to meet all the criteria of said invention. For example, it is possible to use simple physical mixtures, not meeting the requirements of the particle size thereof.

 In another embodiment it is possible to treat the effluent of the treatment with the nickel adsorbent, with the said metal oxide, preferably in a
25 bed thereof.

 In both embodiments, the effect is a further improved and more reliable sulfur removal.

 The removal of the contaminating sulfur compounds is preferably done at a hydrogen partial pressure is between 0.1 and 200 bar and preferably
30 between 10 and 75 bar and more in particular between 30 and 50 bar. The

temperature is preferably between 50 and 300 °C, preferably between 100 and 200 °C.

The process is preferably carried out with an LHSV between 0.1 and 10 hr⁻¹, whereas the GHSV preferably lies between 50 and 5000 hr⁻¹.

5 The adsorbent may be prepared by a process wherein a passivated nickel adsorbent material containing oxidic nickel, optionally on a support or in the presence of a structural promoter, is reduced with hydrogen at a temperature between 100 and 200°C, followed by treatment of the surface of the reduced material with sulfur or a sulfur compound, preferably in an inert
10 solvent, to yield the nickel adsorbent as defined hereinabove. In case a nickel adsorbent is prepared directly from a nickel oxide precursor, without prior reduction and passivation, as above, the temperature of reduction is preferably between 100 and 500°C.

 The sulfur compounds to be used are preferably aromatic sulfur
15 compounds, such as di-benzo-thiophene, 2-methyl thiophene, benzothiophene or dimethyl thiophene. It is also possible to use sulfur powder, polysulfide and the like. The treatment encompasses preferably precipitating S, a polysulfide or an S-compound on the nickel adsorbent, or impregnating the nickel adsorbent with S, a polysulfide or an S-compound sulfur compound. Co-
20 precipitation of the catalyst including the sulphur as described in US-A 5,223,470 is also a possibility. An advantage of this latter process is the improved activity of the final nickel adsorbent. This process includes a step of coprecipitating a precursor for the adsorbent from a solution containing nickel, optionally a dissolved or solid support or structural promoter precursor
25 material and a sulfur compound, and calcining and/or passivating the precipitated material.

Example 1

A 60 wt.% nickel on silica adsorbent was prepared by co-precipitation. Sulphur was added in the precipitation step as a sulphide salt.

- 5 The precipitate was washed with de-ionized water and filtered. The filter-cake was dried and calcined. The calcined material was extruded into 1/16" trilobes. The extrudates were dried, calcined and reduced/stabilized.

- The product is adsorbent B and contained 60 wt.% Ni and 2.75 wt.% Sulphur. Adsorbent B was evaluated in the tetralin activity test after
10 reduction in hydrogen at 425°C for 2 hours and had a rate constant of 0.0085 1/s.g(cat.) at 150°C. The amount of metallic nickel in the adsorbent was 30 %, calculated on the total amount of nickel.

15 Example 2

- A 60 wt.% nickel extrudate (reduced and passivated) was applied as the base adsorbent. This material was loaded in a reactor and treated with a paraffinic solvent containing 100 ppm Sulphur as di-benzo-thiophene. The
20 adsorbent was treated at 150°C and 30 bar hydrogen pressure. At LHSV 10 1/hr; GHSV 1500 1/hr the treatment was monitored measuring the DBT content in the effluent. Once the effluent sulphur content and the feed sulphur content were constant the treatment was considered as finished. Next the adsorbent was dried. The adsorbent obtained is adsorbent A

- 25 Adsorbent A was loaded in a fixed bed reactor and applied in the desulphurization of benzene. The feed contained 4.0 wt-ppm S as thiophene. The conditions were as follows: LHSV 2 1/hr; GHSV 500 1/hr.

The results at 170°C were as follows:

Pressure 10 bar

- 30 92.5 % removal or 308 ppb S in the product

Pressure 20 bar

98.5 % removal or 59 ppb S in the product

5 Pressure 40 bar

99.6 % removal or 28 ppb S in the product

Under the above conditions no benzene hydrogenation activity was observed.

10 Example 3

Adsorbent A was loaded in a fixed bed reactor and applied in the desulphurization of benzene that contained additionally 1000 wt-ppm Styrene. Styrene is a typical component in crude benzene and causes often fouling problems, due to polymer formation on the catalyst surface. The feed contained 4.0 wt-ppm S as thiophene.

The conditions were as follows: LHSV 2 l/hr; GHSV 500 l/hr

20 The results at 150 °C and 40 bar pressure are as follows:

| | |
|--------------------|--------|
| Benzene conversion | 0 % |
| Styrene conversion | 100 % |
| Thiophene conv. | 99.0 % |